

CORRELATION OF CHEMICAL COMPOSITION OF EXTRA HEAVY OILS WITH INCIPIENT COKE FORMATION USING HOT-STAGE MICROSCOPY

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INTRODUCTION

Upgrading bitumen to more valuable products involves a host of chemical reactions. The conversion of relatively low-value bitumen to high-value transportation fuels is usually limited due to coke formation. Bannayan et al. (1) discussed possible mechanisms for deposit formation in the reactor recycle cup and vacuum tower of a commercial unit. These authors proposed asphaltenes to be the cause of vacuum tower fouling in the H-oil unit.

In this study we investigated the coking propensities of extra heavy oil fractions from Athabasca bitumen vacuum bottoms. Athabasca bitumen vacuum bottoms (+524°C) was fractionated into 10 sub-fractions using pentane as super-critical solvent. The super-critical fluid extraction technique allowed the pitch (+524°C) to be extracted into narrow boiling point cuts with different chemical compositions. The development of mesophase was followed using hot-stage microscopy. The coking tendencies (the onset of mesophase formation) of these extra heavy oil fractions are correlated with their chemical compositions. The data from the hot-stage microscopy are also compared with the results obtained from autoclave studies of these fractions. The advantages and limitations of hot-stage microscopy for studying the hydrocracking behavior of heavy oils are discussed.

EXPERIMENTAL

Super-critical fluid extraction (SCFE) of Athabasca bitumen vacuum bottoms (+524°C) into 10 fractions was performed at the State Key Laboratory of Heavy Oil Processing (SKLHOP) of the Petroleum University at Beijing, China. The details regarding the preparation of narrow fractions of petroleum residue using SCFE have been described elsewhere (2). Hot-stage microscopy was carried out on all 10 fractions. In this paper, we report hot-stage and autoclave experiments on selected fractions whose properties are shown in Table 1. The details regarding development of the technique have been described elsewhere (3). The system was pressurized with H₂ (750 psi) and the flow of the gas was maintained at 35 mL/min during the experiments. The most critical factors in mesophase formation are temperature, residence time, heating rate, gas flow rate, and stirring rate (4). In this study, the feedstocks were heated from room temperature to 440°C at 11°C/min. The amount of material used varied between 5 and 12 mg depending on the nature of the fractions (liquid or powder form). Once at 440°C, the experiment was continued for about 3 h. Due to limitations of the experimental setup the samples were not subjected to stirring. The cooling effect of the flowing gas made it necessary to adjust the furnace temperature upward by approximately 50°C to maintain the appropriate sample temperature. This was confirmed by determining the melting points of K₂CrO₇ and Zn. The process was recorded by a video cassette recorder (VCR) for further observations. Mesophase diameter and growth with time were measured periodically using a micro scaler device. Photomicrographs were taken in polarized light under cross polars to show the optical texture of mesospheres and isochromatic regions. Combined magnification was 200X.

In order to compare the coking propensity of the heavy oil fractions obtained from hot-stage microscopy to those obtained from the autoclave, a series of experiments were carried out using fractions 1, 2B, 4, 7, and 9. Hydrocracking experiments were performed at 440°C, 2000 psi H₂ (13.9 MPa) for 30 min using a microautoclave. Hydrogen flow rate was constant at 3 L/min for all the experiments. Autoclave results are shown in Table 2.

Hydrocarbon-type analyses of maltene fractions from the selected samples were carried out before and after autoclave experiments to determine the reaction chemistry at the hydrocracking conditions. These results are shown in Table 3. The detailed experimental setup and hydrocarbon-type analyses were reported earlier (5).

RESULTS AND DISCUSSION

Autoclave results

The results are shown in Table 2. Fractions 1, 2B, 4, and 7 contain no asphaltenes. However, the amount of polar materials in these fractions increased from 9.25 wt % in fraction 1 to 22.61 wt % in fraction 7 (Table 3). Although only a negligible amount of coke (methylene chloride insolubles) was formed from fraction 1 (0.03 wt %), coke formation from fraction 7 was significantly higher (1.4 wt %). Asphaltenes were also produced in all fractions ranging from 2.67 wt % in fraction 1 to 28.38 wt % in fraction 7. Thermal reaction of fraction 9 produced a relatively large amount of coke as well as 45.94 wt % pentane-soluble maltenes. The data indicate that fractions having higher molecular weight, MCR, and aromaticity are more prone to coke formation. These results also confirm the proposed reaction mechanism for coke formation as:



In order to investigate the reaction chemistry in more detail, the maltene fractions in the feedstocks and the products were separated into saturates (M1), mono/diaromatics (M2), polyaromatics (M3), and polars (M4). Significant amounts of saturates were produced, in part, at the expense of polyaromatics and polars (Table 3). The results may indicate that dealkylation reactions are major reaction paths leading to products under the thermal conditions employed. Possible mechanisms for dealkylation are ipso attack by hydrogen radicals (6) and electron transfer from aromatic rings to metal porphyrins present in the tar sand fractions (7). Analysis of the reaction products under way indicates that dehydrogenation of cycloparaffins is also a major reaction leading to products having significantly higher aromaticity than the feedstocks.

Hot-stage microscopy results

When an organic material such as pitch is heated to temperatures between 350°C and 500°C, decomposition and polymerization reactions result in the formation of polycondensed aromatic hydrocarbons which eventually leads to mesophase. Upon further heating, mesophase spheres coalesce to form bulk mesophase and coke having different textures (4). Although hot-stage microscopy was carried out on all 10 SCFE fractions, in this paper we will discuss only the results obtained from fractions 1, 2B, 4, 7, and 9. Observations of hot-stage microscopy experiments are described below. The stated times are referenced to the beginning of the experiments which is taken as time zero (room temperature).

Fraction 1: Due to the high volatility of this fraction no mesophase was observed.

Fraction 2B: Tiny mesophase appeared approximately after 65 min. Mesophase diameter grew from 4 to 30 microns after 84 min (Figure 1a). The growth continued forming particles of more than 50 microns diameter after 94 min. Coalescence of mesophase accelerated and large isochromatic areas (>100 microns) showing domain anisotropy formed after 105 min (Figure 1b). Even at this time smaller mesospheres (< 10 microns) were forming in the isotropic matrix (Figure 1b). By 116 min, the entire field of view was covered by coke with domain anisotropy. Upon termination of experiment, the temperature of the cell decreased rapidly (from 440°C to 410°C in one minute). At the lower temperature it was observed that the previously isotropic areas had become anisotropic due to the reappearance of mesophase. When the residue in the cell was reheated to 440°C the anisotropic texture was converted to isotropic. This confirms the presence of a soluble and fusible mesophase in this fraction and shows that the phase change is reversible with temperature. This phenomenon was reported on hydrogenated coal tar pitch by Honda (4). Due to the high volatility of fraction 2B, the reproducibility of mesophase formation time was poor. Less volatile fractions (fractions 7 and 9) showed better reproducibility.

Fraction 4: Mesophase first appeared after 105 min. The growth of the spheres was as follows: 4 microns after 106 min, 9 microns after 116 min, and 33 microns after 127 min. Growth and coalescence of mesophase resulted in the formation of larger mesophase (>50 microns) after 136 min (Figure 1c). After 166 min the mesophase particles had formed a "donut-shaped" structure surrounded by mesospheres of various sizes and shapes (Figure 1d). When the residue was cooled and reheated to 440°C the same behavior as fraction 2B was observed.

Fraction 7: The time of mesophase formation was 70 min. Mesophase spheres grew from 3 microns in diameter after 74 min to 21 microns after 98 min (Figure 1e) and finally formed large coke areas with flow domain anisotropy after 153 min (Figure 1f). The flow domain was observed only in this fraction. The flow domain texture enclosed smaller patches of isotropic matrix, which, in itself, contained numerous tiny mesospheres (1-2 microns in size). The disc-like inclusions of isotropic pitch

surrounded by anisotropic pitch are similar to the results reported by Hüttinger et al. (8). Complete conversion of this isotropic phase to coke could take place only after a long time at 440°C. The behavior of this fraction in forming flow domain warrants further investigation.

Fraction 9: The first mesophase spheres were noticed after 57 min which is faster than any of the other fractions examined. After 95 min the sample had developed large isochromatic areas with domain anisotropy and rounded margins (Figure 1g). After 104 min some small mesophase spheres could still be seen floating in an isotropic matrix. The resulting coke was angular with serrated edges (Figure 1h). Upon cooling, these isotropic areas became anisotropic with a mosaic texture, which is consistent with observations in previous samples. When the residue was cooled and reheated to 440°C the same behavior as fractions 2B and 4 was observed.

The above data indicate that the incipient mesophase formation is dependent on the chemical composition of the fractions. For instance, the chemical analysis of fraction 9 (Table 1) indicates that this fraction contains 88.0 wt % asphaltenes and has the highest molecular weight, aromatic carbon, and MCR. Compared to the more aliphatic fractions 2B and 4, the molecules in fraction 9 require shorter heating time to become the lamellar molecules which eventually are involved in mesophase formation. Thermal hydrocracking of this fraction in the autoclave also produced the highest coke yield (Table 2). Overall, the results of hot-stage microscopy are consistent with the autoclave experiments for fractions 4, 7, and 9. Fraction 2B produced the least amount of coke in the autoclave runs. However, the time of mesophase formation for this fraction in the hot-stage run was earlier than expected. This was attributed to the fact that this fraction is relatively volatile and, under hot-stage conditions, evaporated significantly leaving the most refractory components behind.

The second important observation that can be related to the chemical composition of the fractions is the relative rate of mesophase formation at 440°C. Mesophase growth rate as a function of time was recorded for fractions 4 and 7. It was observed that in fraction 4 the growth rate was slower in the first 60-75 min at isothermal temperature (440°C) followed by much faster growth. In contrast, fraction 7 showed a continuous linear growth rate. These observations indicate possible differences in the reaction kinetics of the two fractions which, in turn, relates to the differences in their chemical compositions (Table 1). Fraction 9, being the most refractory according to the chemical characteristics, showed the highest rate of growth compared to the other three fractions examined. Accordingly, it was observed that mesophase growth was faster in the first 40-45 min of formation at isothermal temperature. These results are in agreement with data reported by Hüttinger et al. (8).

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Figure 1

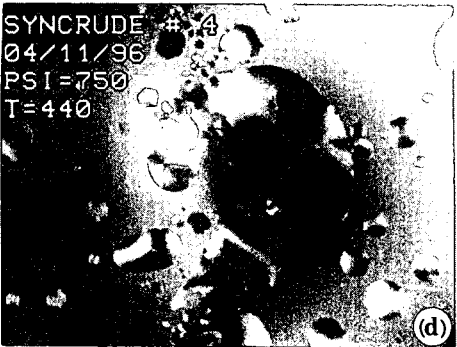
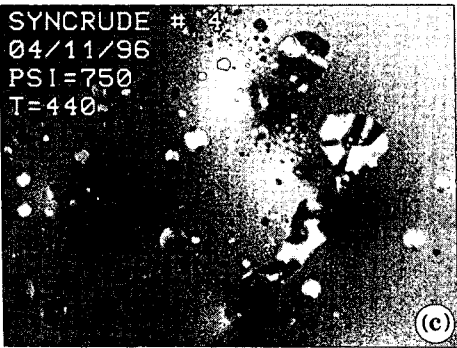
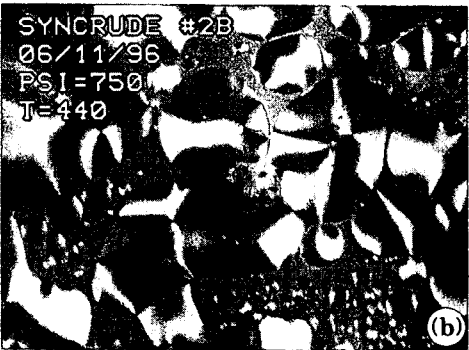
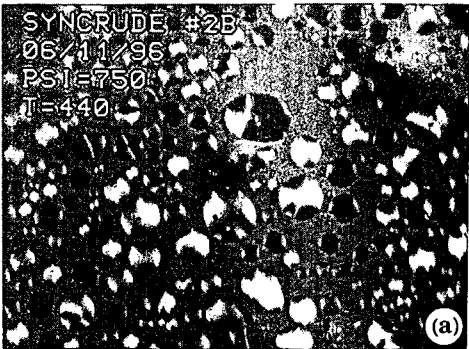
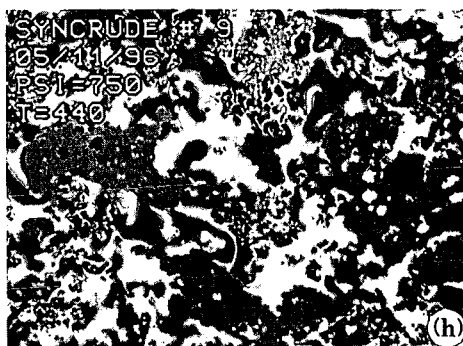
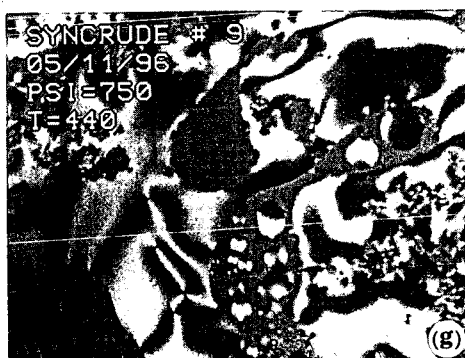
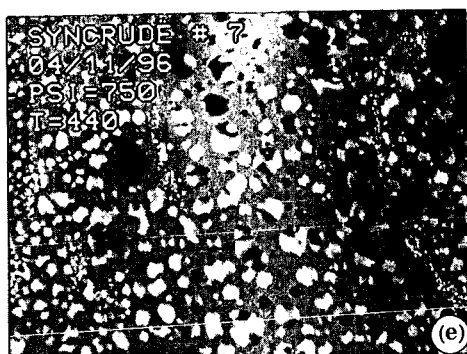


Figure 1



Description of photomicrographs

- (a) Fraction 2B- Growth of mesophase spheres from isotropic matrix after 84 min.
- (b) Fraction 2B - Coalescence of mesophase spheres after 105 min.
- (c) Fraction 4- Growth of mesophase spheres from isotropic matrix after 136 min.
- (d) Fraction 4- Coalescence of mesophase to 'donut' shape structure after 166 min.
- (e) Fraction 7 - Formation of mesophase from isotropic matrix after 98 min.
- (f) Fraction 7 - Development of flow domain and domain anisotropy after 153 min.
- (g) Fraction 9 - Formation of mesophase and coke with domain anisotropy after 95min.
- (h) Fraction 9 - Coke with angular and serrated texture after 104 min.

Table 1 - Characteristics of Athabasca bitumen vacuum bottoms fractions obtained by SPCE technique

Fraction #	1	2B	4	7	9
Pressure, MPa	4-5	5.5-6	7-8	10-11	>12
Wt% of pitch	12.7	7.6	6.5	2.6	40.4
Density, g/ml @20°C	0.9745	1.0061	1.0427	1.0678	N/a
Molecular weight, g/mol	506	711	825	1209	4185
Sulphur, wt %	4	5	6	6.8	7.6
Nitrogen, ppm	3080	4330	6160	7530	10500
Carbon, wt %	84.5	83.5	83	83	78.5
Hydrogen, wt %	11.5	10.95	10.25	9.7	8
C/H (atomic)	0.612	0.635	0.675	0.713	0.818
Aromatic carbon*, %	26	25	36	43	49
Nickel, ppm	12.8	30.1	71.1	138	339
Vanadium, ppm	30.7	69.8	166	355	877
MCR, wt %	5.64	10.83	18.16	26.46	48.94
Saturates, wt %	26.86	9.68	1.36	0.28	0
Aromatics, wt %	57.23	65.7	63.86	45.91	2.19
Resins, wt %	15.91	24.62	34.78	53.81	9.38
Asphaltenes, wt %	0	0	0	0	88.03

*¹³C NMR

Pitch = +524°C fraction

Table 2- Thermal hydrocracking products (wt %) of selected fractions

Fractions	Gases	Coke	Asphaltenes	Maltenes
1	14.61	0.03	2.67	82.69
2B	14.15	0.09	10.54	75.22
4	12.34	0.12	22.08	65.08
7	13.47	1.40	28.38	56.75
9	12.98	8.68	32.40	45.94

Maltenes = pentane solubles

Asphaltenes = pentane insolubles

Coke = methylene chloride insolubles

Table 3. Hydrocarbon-type distribution (wt % of feed) of selected fractions before and after thermal hydrocracking

fraction	feed				product			
	M1	M2	M3	M4	M1	M2	M3	M4
1	15.08	9.63	66.04	9.25	30.39	10.65	36.05	5.60
2B	5.29	5.29	75.02	14.40	23.64	9.80	36.81	4.97
4	2.34	1.08	73.97	22.61	18.24	8.62	33.83	4.39
7	0.06	0.08	72.66	27.20	18.90	6.61	27.67	3.58
9	Approximately 88 wt% asphaltenes				17.16	4.80	20.61	3.37

M1 = saturates
M2 = mono/diaromatics
M3 = polyaromatics
M4 = polars